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The invention relates to a oligodynamische surface coating for a metallic substrate with the features specified in the preamble of Claim 1 as well as a method to the production of such surface coatings with the features specified in the preamble of Claim 11.

Traces of heavy metals affect various microorganisms growth-retarding or killing. The oligodynamische metal effect can be proven to for example good in the agar diffusion test, becomes occupied with which a test plate with certain metals and/or metal compounds, seeded with staphylococci. After a Vordiffusion, with which ensured is to become that a sufficient large amount of the single metals goes into solution, breeds one the colonies a predetermined period out. Subsequent observed one that around some coins a "restraining zone" developed, suppressed perfect in which a growth of the staphylococci hindered or becomes. The material classes of the germ-damaging agents cover in particular heavy metals such as cadmium, silver, copper and mercury (see Wallhäusser, K. H., Schmidt, H.: Sterilization, disinfection, preservation, chemotherapy, George Thieme publishing house Stuttgart 1967, side 102 to 106). The oligodynamische effect finds use in technical ranges, in which the growth of microorganisms and funguses hindered and/or the microorganisms killed to become to be supposed. Thus for example the European patent application shows 0,636,375 A1 the use of silver, coppers or their alloys in the range of the surfaces of equipment and sanitary articles, which come with the human skin into contact.

An other technical field, become the used on which biocides and fungicidal properties of heavy metals, lies in the ventilation and building of air conditioning systems. Like that known is to provide the surfaces of such plants, which come with air into contact, with a gold coating from the DE 40 14 087 C2.

With air conditioners of automobiles special requirements exist to the micro biocides effectiveness of the surface coating.
▲ top In the foreground with the fact the problem stands that after longer downtime and renewed switching on of the air conditioner on for short time an unpleasant can become more modriger, muffiger odor perceived. The reason for a such smelling nuisance is to be looked for among other things in the deposition of smallest particles different origin on the evaporator lamellas of the air conditioner. In particular microorganisms and funguses settle on the evaporator lamellas, whose katabole Stoffwechselprodukte cause the unpleasant odors.

In the switched on state of the air conditioner from the outside introduced air flows through or with rotating enterprise the air the continuous evaporator of the air conditioner circulated in the vehicle interior. Due to the air flow a continuous adsorption and desorption procedure take place at the surfaces of the evaporator, whereby the adsorption outweighs first. This leads the evaporator of accommodating housing to a lining formation on the air-washed surfaces of the evaporator and on the inside. In this coating ordinary smell-intensive components are contained, whose concentration is not sufficient alone yet to cross the smell threshold with which a significant unpleasant smell feeling caused become. By the strengthening effect of microorganisms, which likewise settle on the coating, this smell threshold however significant can be crossed. In out or switched on state of the air conditioner adsorption and desorption become essentially maintained in an equilibrium state. In the off state however the concentration of smell-intensive fabrics rises due to the metabolic activity of the microorganisms gradual. If the air conditioner is again switched on, then the concentration of the smell-intensive fabrics for a short time lies above the threshold value perceptible for the vehicle occupants. There is therefore surface coatings for the interior-flat of air conditioners developed, with which smell-causative microorganisms and funguses killed or its growth prevented is to become.

From the DE 197 50 128 A1 it is known to cover for surfaces with metallic copper a contained layer. The copper layer becomes applied thereby by means of an electrochemical process galvanic, electroless or by means of metal deposition in a cuprous salt bath.

In US 5.366.004 will proposed to lay a color on at exposed site in the air conditioner. The color contains coppers, silver, copper salts, silver salts and/or zinc salts.

Another proposal becomes in the DE 197 48 256 A1 described, becomes applied with which on the evaporator of the air

conditioner and/or on the interior surface the evaporator of accommodating housing a thin layer with a oligodynamisch effective heavy metal. As heavy metal and/or heavy metal compound silver and copper salts become mentioned.

In the German application DE 197 50 122 A1 the surface with a metal or a metal compound finally becomes from the group of the noble and half precious metals coated. That micro biocide effective fabric becomes powdery introduced into a lacquer layer.

The known solutions exhibit the disadvantage that those are biocide and fungicidal acting heavy metal particle production-determined relative large and diameters of 20 mu m and more exhibit. Thus also an interface between air, water and the metal is reduced. Only if the metal at the interfaces can cross into the other phases, the oligodynamische effect occurs. Therefore relative large amounts at heavy metals become required, which lets the material costs and late disposal costs rise.

An other problem with the establishment of oligodynamischen surface coatings on heavy metal basis represents the corrosion protection of the metallic substrate. At the phase boundaries local cells are formed between that relative large heavy metal particles and the metallic and generally substrate existing which can be coated from a unedleren metal. The corrosion protection the surfaces must become therefore passivated before and/or the coating must anti-corrosive acting additives contain.

The DE 198 13 709 A1 points a method out, with which the metallic substrate before corrosion can become protected by application of a surface coating. In addition provided, based on the metallic substrate matrix is, on (hetero) - polysiloxane on to lay. That matrix becomes species added, which with before corrosion to protective metal the responsive and a reaction product form, which exhibit a more negative education enthalpy than a corrosion product of the metal. With the being present of the thermodynamic sturdier compound are among other things corrosion causative species, like oxygen, waters and hydrogen sulfide, which is extracted reaction partners. Is to be taken furthermore from the writing to attach to the interference of the properties of the coating other components. To the improvement of an abrasion resistance provided, nanoskalige particles from the group of the oxides, oxide hydrates and carbides of silicon are to mix aluminium and boron as well as the transition metals with the production of the coating composition in form of a powder. It is unimportant to complete thereby whether those can react to anti-corrosive acting species with these fabrics or step into interaction. With the enumerated materials is to be counted on a passivation of the surfaces nano-potash towards particles. Further disclosed is to add organic non-columnar of the coating composition in this writing if the starting material has groupings, who are a polyaddition and/or a polycondensation reaction accessible. Also a modification of the starting compounds in such a manner that these groupings cover, who are a polyaddition, a polymerization and/or a polycondensation reaction accessible become shown. In particular hydrophobic, oleophobe and dirt-deflecting properties as well as the scratch resistance are to be improved by the integration of polymeric structures.

Object of the instant invention is it, a oligodynamische surface coating for a metallic substrate, in particular for metallic interior-fiat of an air conditioner of automobiles to create it the allowed to prevent inexpensive and durably with an high efficiency an occupancy of the metal surfaces with microorganisms and funguses and the simultaneous metallic substrate before corrosion protects.

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This object by the oligodynamische surface coating with the features specified in the claim 1 as well as the method become according to invention the production of the coating with the features dissolved specified in the claim 11. The surface coating is characterised by the fact that it exhibits at least the subsequent components:

a) matrix on basis of (hetero) - polysiloxanes, which are producible by hydrolysis and condensation processes and a permeability opposite water and ions possess, and/or
b) nanoskalige heavy metal particles, which are in above matrix embedded in particular, and optional
c) a corrosion inhibiter, which steps at the surface of the substrate with the metal to the formation of a corrosion protection layer responsive or in interaction, however opposite the heavy metal nano-potash towards heavy metal particle is as far as possible unreaktiv.

Thus a system is provided, which becomes fair both the requirements at biocides and/or fungicidal effect, and the corrosion protection. The permeability that matrix a possible diffusion at the phase boundary with air/water by oxidation resultant heavy metal ions to the desired effect place. By addition of the corrosion inhibiters simultaneous prevented becomes that corrosive processes on the surface of the metallic substrate can take place. Beyond that it has itself shown that the achieved with the help of the matrix mentioned a stabilization becomes nano-potash towards heavy metal particles against agglomeration. Only by it nanoskalige heavy metal particles stand durably and in controlled mass of an use in the range of the fight against microorganisms and funguses open.

Preferably the heavy metal particles consist of or several side group elements, in particular noble metals. Particularly prefered is thereby the use of silver and/or coppers. By the integration nanoskaliger heavy metal particle into the surface coating can be increased the boundary surface range between metal, air and water, so that the oligodynamische effect in the range of the coating is improved. As metallic substrates comes in particular aluminium or its alloys into question. A layer thickness of the surface coating is appropriate preferably within the range of 1 to 50 mu m, in particular for 1 to 20 mu m, particularly prefered 2 to 10 mu M.

Beside the invention-essential properties of the surface coating (protection before corrosion and agglomeration,

oligodynamische effect) that can become matrix also properties such as abrasion resistance, color, scratch resistance, thermal conductivity and hydrophilicity affected by targeted modification. So preferably provided can be that those matrix organic cross-linking structures included, which by integration of condensation and/or additionable, functional groups into the starting compounds to the production (hetero) - polysiloxanes and their addition and/or condensation with suitable organic non-columnar are producible. Likewise it is more conceivable that those matrix polymere, organic structures included. Such structures can be manufactured by integration of polymerization, polycondensation and/or polyadditionable, functional groups in the starting compounds and their polyaddition, polymerization and/or polycondensation with suitable monomers.

After the method a Beschichtungssol becomes on the metallic workpieces applied and cured, those the components mentioned included the production of the oligodynamischen surface coating. The Beschichtungssol becomes by immersion, injecting or over other wet-chemical methods on the substrate applied. Hardening can take place thermal and/or photochemical.

Other prefered aspects of the invention result from the remaining features specified in the Unteransprüchen.

The invention becomes subsequent explained near in an embodiment.

In accordance with the embodiment an air conditioner of a motor vehicle in the range of its interior surface, in particular in the range of the evaporator, is to be provided with a oligodynamischen surface coating. Evaporators of air conditioners are predominant made from aluminium alloys. On the interior surface of the evaporator become after the invention process a very thin, water and a ion-permeable (whereby a diffusion permeability is already sufficient), polymeric coating applied. The polymeric coating based on one (hetero) - polysiloxane (matrix), whose illustration in the other one becomes still near explained. The production of the coating a Beschichtungssol becomes cured on the ranges of the evaporator which can be coated applied and thermal and/or photochemical (for the example bottom UV or IR irradiation).

Nanoskalige heavy metal particles from silver and/or coppers are mixed to the Beschichtungssol. In each case a composite between that forms for matrix and the heavy metal particles. The surface coating possesses a layer thickness of maximum 50 mu M. after application and cure and/or penetration. The coating becomes so conducted that a weight of the heavy metal particles is appropriate for that in a range from 0,1 to 60% related to a total weight matrix.

Those that matrix at the basis located (hetero) - polysiloxanes preferably lead themselves from at least an hydrolysable Silizium-Verbindung of the general formula
R4-xSiR'x (I)
off, where the remainders R represent same or various hydrolytic split offable remainders. More conceivable are for example halogens or Alkoxy, Acyloxy or Aminosubstituenten. Of course also different, the person skilled in the art can become known hydrolysable Silizium-Verbindungen used. The illustration and conversion of these and also the starting compounds modified in the other one is known and becomes therefore in the other one near not explained. By hydrolysis and condensation reactions an inorganic polymer - the desired (hetero) - can be produced to polysiloxane -. A degree of crosslinking, polymerization degree and other morphologic properties are in far mass the variable.

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The substituent R' can be optional into the desired starting compound integrated (x can be therefore also 0). It is characterised by the fact that it is not a substitution reaction at the silicon accessible. The keeping of an high cross-linking and polymerization degree of the inorganic polymer x becomes prefered 1 limited on x =.

The grouping R' is to serve in particular to take up organic cross-linking structures to the matrix with. In addition the remainder R' carries condensation and/or additionable, functional groups. From reaction with suitable organic non-columnar, as for example polyepoxides, polyols or aromatic polyols, the desired structures result, whereby an initiator for the organic crosslinking must become added if necessary. Also such a proceeding is sufficient from the state of the art known.

Further the remainder R' can contain functional groups, which are polymerization, polycondensation and/or polyaddition reactions accessible. By conversion with suitable monomers the morphologic properties of the coating can become in almost arbitrary manner modified. In the foreground it stands however in each case that the coating exhibits a finite permeability for ions and water molecules, so that biocides and fungicidal active ingredients (the heavy metal ions) can diffuse the surface of the coating to the effect place thus.

Particularly suitable starting compounds for the Beschichtungssol in mentioned above the sense are in particular 3-Aminopropyl-triethoxysilan (APTS) or 3 (triethoxysilyl) propylbernsteinsäureanhydrid. The latter can be hydrolisieren and/or condensed to bottom addition of catalytic quantities of an acidic one (for the example phosphoric acid).

The Beschichtungssol included furthermore a corrosion inhibiter, the one passivation of the surface of the metallic substrate opposite corrosive acting substances possible. The corrosion inhibiter must become thereby however so selected that it is as far as possible unreaktiv opposite the heavy metal nano-potash towards heavy metal particle, so that the oligodynamische effect is not limited. Usually it concerns with the corrosion inhibiters oxidizing agents, which oxidize the metallic substrate at its surface, whose oxidation ability is not sufficient however, in order to react with the heavy metals nano-potash towards particles. With the reaction with the metal of the substrate it is to come to the formation of a corrosion protection layer, as the reaction product is more stable on the one hand almost insoluble and on the other hand

thermodynamic than possible corrosion products. So for example the formation of mullite, kaolinite, Kyanit, Diaspor or aluminium phosphate is by reaction with the corrosion inhibiter prefered in case of the substrate here based on aluminium. The corrosion inhibiter can to (hetero) - polysiloxanes bonded its (for the example over covalent bond) and only molecular-disperse in the Beschichtungssol to be present and with the cure of the same in the inorganic skeleton entrapped become. It must become only ensured ones that a direct contact with the metal and a reaction are and/or interaction between the corrosion inhibiter and the metal of the substrate possible. Particularly suitable corrosion inhibiters are sodium benzoate or phosphoric acid.

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1. Oligodynami surface coating for a metallic substrate, in particular for metallic interior-flat of an air conditioner of automobiles, characterised in that the surface coating at least the subsequent components exhibits:

a) matrix on basis of (hetero) - polysiloxanes, which are producible by hydrolysis and condensation processes and a permeability opposite water and ions possess, and/or
b) nanoskalige heavy metal particles, which are into matrix an embedded, and optional
c) a corrosion inhibiter, which steps at the surface of the substrate with the metal to the formation of a corrosion protection layer responsive or in interaction, however opposite the heavy metal nano-potash towards heavy metal particle is as far as possible unreaktiv.

2. Surface coating according to claim 1, characterised in that the heavy metal particles of or several side group elements, in particular noble metals, consist.

3. Surface coating according to claim 2, characterised in that the heavy metal particles from silver and/or coppers exist.

4. Surface coating after one of the claims 1 to 3, characterised in that a weight of the heavy metal particles in a range from 0,1 to 60% related to a total weight that matrix lies.

5. Surface coating after one of the claims 1 to 4, characterised in that the layer thickness of the surface coating 1 to 50 mu m amounts to.

▲ top 6. Surface coating according to claim 5, characterised in that the layer thickness of the surface coating 1 to 20 mu m amounts to.

7. Surface coating according to claim 5, characterised in that the layer thickness of the surface coating 2 to 10 mu m amounts to.

8. Surface coating after one of the claims 1 to 7, characterised in that the metallic substrate from aluminium or an aluminium alloy exists.

9. Surface coating after one of the claims 1 to 8, characterised in that the matrix organic cross-linking structures included, which by integration of condensation and/or additionable, functional groups into the starting compounds to the production (hetero) - polysiloxanes and their addition and/or condensation with suitable organic non-columnar are producible.

10. Surface coating after one of the claims 1 to 9, characterised in that the matrix polymere, organic structures included, which by integration of polymerization, polycondensation and/or polyadditionable, functional groups into the starting compounds to the production (hetero) - polysiloxanes and their polyaddition, polymerization and/or polycondensation with suitable monomers are producible.

11. Method to the production of a oligodynamischen surface coating for a metallic substrate, in particular for metallic interior-flat of an air conditioner of automobiles, characterised in that on one surface of the metallic substrate a Beschichtungssol applied and cured which can be covered becomes, which on one (hetero) - polysiloxane of based and/or nanoskalige heavy metal particles as well as an optional corrosion inhibiter included, which step at the surface of the substrate with the metal to the formation of a corrosion protection layer responsive or in interaction, however opposite the heavy metal nano-potash towards heavy metal particle are as far as possible unreaktiv.

12. Process according to claim 11, characterised in that nano-potash towards heavy metal particles from or several side group elements, in particular noble metals, exists, which are nobler than the metal of the substrate.

13. Process according to claim 12, characterised in that nano-potash towards heavy metal particles from silver and/or coppers exists.

14. Process according to claim 12, characterised in that the metallic substrate from aluminium or an aluminium alloy exists.

15. Process according to one of claims 11 to 14, characterised in that the application of the coating brine by immersion, injecting or over other wet-chemical methods made.

16. Process according to one of claims 11 to 15, characterised in that hardening the coating brine thermal and/or photochemical made.

17. Process according to one of claims 11 to 16, characterised in that (hetero) - polysiloxanes with polymerization, polycondensation and/or polyadditionable, functional groups used will become and by polyaddition, polymerization or polycondensation with suitable monomers the establishment of polymere, organic structures in that matrix reacted.

18. Process according to one of claims 11 to 17, characterised in that (hetero) - polysiloxanes with condensation and/or additionable, functional groups used will become and by addition and/or condensation with organic non-columnar the establishment organic cross-linking structures in that matrix reacted.

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